

**OFFICE OF NAVAL RESEARCH
END-OF-YEAR REPORT
PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS/STUDENT REPORT**

for

Grant: N00014-95-1-0731

R&T Code: 3135043---03

Group III Materials: Molecular Design of New Phases with Applications in Electronics and
Optoelectronics

Andrew R. Barron

Rice University

Department of Chemistry,
6100 Main Street, Houston, TX 77005

Date Submitted: 1 July, 1996

Reproduction in whole, or in part, is permitted for any purpose of the United States Government.

This document has been approved for public release and sale, its distribution is unlimited.

19960715 071

OFFICE OF NAVAL RESEARCH
Publications/patents/presentations/honors report

R&T Number: Grant:

Contract/Grant Number: N00014-95-1-0731

Contract/Grant Title: Group III Materials: Molecular Design of New Phases with Applications in Electronics and Optoelectronics.

Principle Investigator: Andrew R. Barron

Mailing Address: Department of Chemistry, Rice University, 6100 Main St., Houston, TX 77005

Phone Number: (713) 737 5610

Fax Number: (713) 737 5619

E-Mail Address: arb@ruf.rice.edu

Web page: pcheml.rice.edu/Faculty
Staff/Barron.html

- a. Number of papers submitted to refereed journals, but not published: 5
- b. Number of papers published in refereed journals: 6
- c. Number of book chapters submitted, but not yet published: 1
- d. Number of book chapters published: 0
- e. Number of printed technical reports/non-referred articles: 0
- f. Number of Patents filed: 3
- g. Number of Patents Granted: 1
- h. Number of invited presentations: 3
- i. Number of submitted presentations: 1
- j. Honors/Awards/Prizes: (see attached)
- k. Total number of full time graduate students and Post-Doctoral Associates supported during this period, under this R&T project number: ____
 - Graduate students: 1 Post-Doctoral Associates: 2including the number of,
 - Female graduate students: 1 Female Post-Doctoral Associates : 1the number of,
 - Minority Graduate students: 0 Minority Post-Doctoral Associates: 0the number of,
 - Asian Graduate students: 0 Asian Post-Doctoral Associates: 0
- l. Other funding: see attached.

Complete Citations and Attachments

Section a.

1. Chemical vapor deposition of gallium and indium selenide nano-particles. S. L. Stoll, E. G. Gillan, and A. R. Barron, *Chem. Vapor Deposition*, in press.
2. A FETISH for gallium arsenide. A. R. Barron, *Mat. Res. Soc., Symp. Proc.*, in press.
3. Tert-*amyl* compounds of aluminum and gallium: halides, hydroxides and chalcogenides. C. J. Harlan, E. G. Gillan, S. G. Bott, and A. R. Barron, *Organometallics*, submitted for publication.
4. Synthesis of Gallium Chalcogenide Cubanes and their use as CVD precursors for Ga₂E₃ (E = S, Se). S. Shulz, E. G. Gillan, L. M. Rogers, R. Rogers, and A. R. Barron, *Organometallics*, submitted for publication.
5. Solid state structure of [(^tBu)₂In(μ-Cl)]_∞: an unusual saw-tooth polymeric structure. S. L. Stoll, S. G. Bott, and A. R. Barron, *Polyhedron*, submitted for publication.

Section b.

1. Group 13-16 precursors: what factors control their volatility? E. G. Gillan and A. R. Barron, *Mat. Res. Soc., Symp. Proc.*, 1996, **415**, 87.
2. CVD of SiO₂ and related materials: An overview. A. R. Barron, *Adv. Mater. Optics Electron.*, 1996, **6**, 101.
3. Photo-assisted chemical vapor deposition of gallium sulfide. P. Pernot and A. R. Barron, *Chem. Vap. Deposition*, 1995, **1**, 75.
4. Gallium and indium compounds of sulfur donor ligands: pyridine-2-thiolates and diphenylthiophosphates. C. C. Landry, A. Hynes, A. R. Barron, I. Haiduc, and C. Silvestru, *Polyhedron*, 1996, **15**, 391.
5. A new cubane MOCVD precursor for gallium sulfide: Structural determinations of [(Et₂MeC)GaS]₄ by X-ray diffraction and [(^tBu)GaSe]₄ by electron diffraction. M. B. Power, D. Hnyk, G. McMurdo, D. W. H. Rankin, and A. R. Barron, *Adv. Mater. Optics Electron.*, 1995, **5**, 177.
6. MOCVD of group III-chalcogenides. A. R. Barron, *Adv. Mater. Optics Electron.*, 1995, **5**, 245.

Section c.

1. CVD of insulating materials. A. R. Barron, *CVD of Nonmetals*, Ed. W. Rees, Jr., VCH (1995).

Section h.

1. Solid State Gordon Conference, New Hampshire- Gallium Sulfide: Molecules and Materials
2. Materials Research Society, Boston - Gallium Sulfide: Molecules and Materials
3. ACS North East Regional Meeting, NY - Gallium Sulfide: Materials Applications
4. Rice University, Department of Mechanical Engineering and Materials Science.
5. SMU, Department of Chemistry - Gallium Sulfide: Molecules and Materials
6. University of North Texas, Department of Chemistry - Gallium Sulfide: Molecules and Materials
7. University of California at Santa Barbara, Department of Chemical Engineering - Gallium Sulfide: Molecules and Materials.

Section h.

1. Inorganic Gordon Conference, New Hampshire, July 1995.
2. MRS meeting, Boston, December, 1995.
3. University of Missouri, St. Louis, 1995.

Section i.

1. MRS meeting, Boston, December, 1995.

j. Honors/Awards/Prizes

1. Corday-Morgan Medal and Prize, Royal Society of Chemistry.
2. Editorial Board, *Advanced Materials*.
3. Editorial Board, *Main Group Metals Chemistry*.

l. Other funding: 6/1/93 - 5/31/96.

1. ONR "Tert-butyl alumoxane", \$90,000.
2. ONR/STTR "Highly Processable Pre-ceramic Polymers", \$ 39,875.
3. Welch Foundation "New High Latent Lewis Acidic Catalysts", \$ 102,000.
4. NSF travel award "Gas phase structures of MOCVD Precursors to Group 13 Materials", \$ 18,000.

End-of-Year Report - PART II

- a. Principle Investigator: Andrew R. Barron
- b. Tel. Number: (713) 737 5610
- c. Cognizant ONR Scientific Officer: Hal Guard
- d. Description of project

We have recently prepared a wide range of gallium sulfide compounds, e.g., [(^tBu)GaS]₄, and not only demonstrated their suitability as MOCVD precursors for GaS thin films *per se*, but also provided unique evidence for the structural dependence of the deposited film upon the structure of the precursor molecule. The goal of this proposal is to expand on these initial results, including the electronic characterization of, and development of applications for, the new cubic phase of GaS. We propose to synthesize new metal-organic chalcogenide compounds of aluminum, gallium and indium, and use them for the growth of group III-chalcogenide thin films. We propose that the film deposition studies will be performed with a view to the growth of non-thermodynamically stable phases. In addition, we propose to investigate the use of molecular control over micro- and macro-scopic structure for the MOCVD growth of quantum confined structures and surface photon traps.

- e. Significant results during the last year.

Recent accomplishments that have resulted from the present ONR research program as a consequence of the formation of the new phase of GaS are as follows:

1. A new hexagonal phase of GaTe and a new cubic phase of GaSe have been grown by MOCVD.
2. High quality InSe thin films have been grown and devices are being constructed.
3. Passivation of ZnSe by GaS and GaSe has been demonstrated.
4. New low temperature precursors for GaS and GaSe have been developed.
5. CVD using compounds in which the M-E bonding is weak results in precursor pre-decomposition and the formation of uniform spherical semiconductor nanoparticles. The parameters controlling nanoparticle formation have been investigated.
6. The structure/volatility relationships of organometallic precursors has been determined. It is hoped that this will enable the design of new precursors with controlled volatility.
7. Scoping experiments have been undertaken to demonstrate the application of cubic-GaS, to electronically-based chemical specific sensors.

- f. Summary of next years plans

1. The formation of nanoparticles of III-VI semiconductors will be investigated with respect to determining the relationship between precursor and decomposition pathway.
2. Our new phases of GaTe and InSe will be investigated to determine the relationship of structure to semiconducting properties. We propose to continue to develop molecular control over solid state structure.
3. Our study of the factors that control an organometallic compound's volatility will be continued. New precursors will be designed.
4. Our work on the fabrication of chemical sensors will continue.

- g. Names of graduate students and Post-doctoral fellows currently working on the project.

Graduate students: Ms. Andrea Keys

Post-doctoral Fellows: Dr. Sarah Stoll and Dr. Edward Gillan

End-of-Year Report - PART III

c. Explanatory text.

(a) The MOCVD growth of group III-VI materials has been investigated, in particular, the growth of meta-stable phases through molecular control. The effects of the relative intramolecular bond strengths, i.e., ME in $[(R)ME]_4$ ($M = Al, Ga$; $E = S, Se, Te$), is found to be a determining factor in the formation of meta-stable versus thermodynamically stable phases. Furthermore, the stability of a precursor molecule is able to control the formation of thin films or nano-particles.

(b) Gallium and indium selenide nano-particles have been grown by atmospheric pressure CVD from the single source precursors $[(^tBu)GaSe]_4$ and $[(EtMe_2C)InSe]_4$, respectively. The InSe thin films consist of spheres. As with the InSe films, those grown from $[(^tBu)GaSe]_4$ consist of pseudospherical nanoparticles, however, unlike the InSe films these appear as "pearl-necklaces" which retain their identity and remain intact after being floated from the growth substrate. The small sizes and pseudo-spherical geometry of the InSe and GaSe particles suggests a vapor phase growth process.

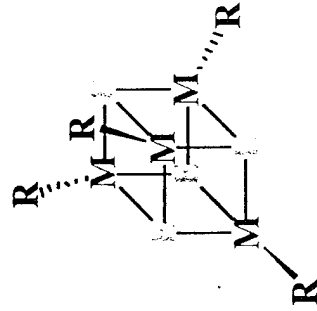
(c) The surface modification of the GaS is being investigated to ascertain the suitability of our GaS/GaAs FETISH as a chemical specific sensor. The proposed research is aimed at providing a simple demonstration that the surface of MOCVD grown GaS can be chemically modified to provide for surface mediated molecular recognition. The chemically modified GaS surfaces are at present being characterized, along with model compounds.

Group III Materials: Molecular Design of New Phases with Applications in Electronics and Optoelectronics

Andrew R. Barron, Rice University

Technology Issues:

- . How does a molecular precursor control the structure of a solid state material
- . Can materials be applied to the fabrication of new devices
- . Passivation of GaAs
- . How can a micro-electronic chemical sensor be fabricated?



Objectives:

- . Understand the envelope of molecular control
- . Design new molecules to control phase
- . Develop new materials for applications
- . Develop new electronic GaS/GaAs based chemical sensors.

Approach:

- . Synthesis of new Group III-VI molecular compounds with stable core structures
- . MOCVD of thin films
- . Gas phase TOF MS and electron diffraction to determine vapor phase species and decomposition
- . Direct application of materials
- . Surface modification of new designed materials for device applications

Accomplishments:

- . Synthesis of new III-VI molecular compounds
- . Growth of non thermodynamic phases of GaS, GaSe, InS and InSe
- . Growth of nano-spheres
- . Demonstration of molecular control
- . Passivation of GaAs
- . Passivation of InP solar cell
- . Passivation of InGaAs laser
- . Fabrication of FETISH

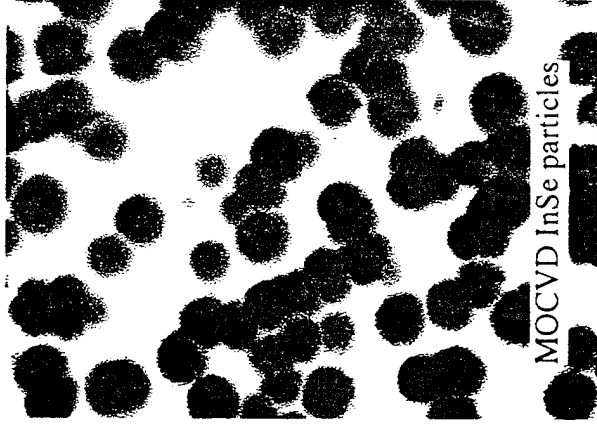
Transitions:

- . Gallia, Inc. has been purchased by TriQuint, Inc. Development of FET applications continues
- . Development agreement with SDL for laser diodes
- . Development agreement with ASEC for solar cell passivation

MOCVD growth of GaSe and InSe nano-particles

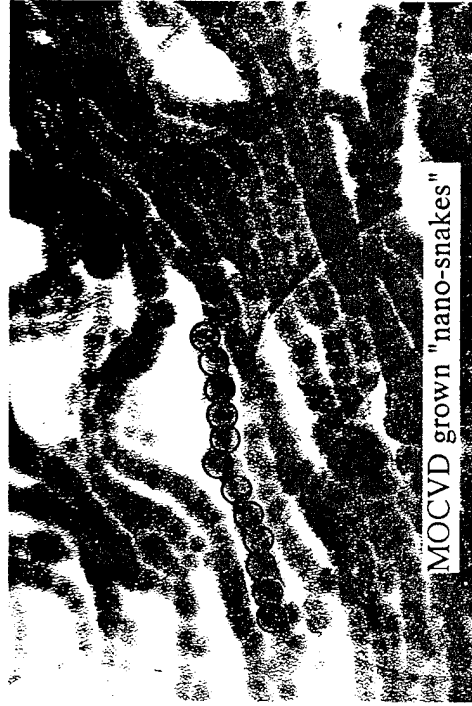
Observation:

- . M_4E_4 core decreases in stability as move down Periodic table
- . M_4E_4 core fragmentation observed for GaSe and InSe cubes
- . Vapor phase not surface decomposition observed for "fragile" cubes



Nano-particles by MOCVD:

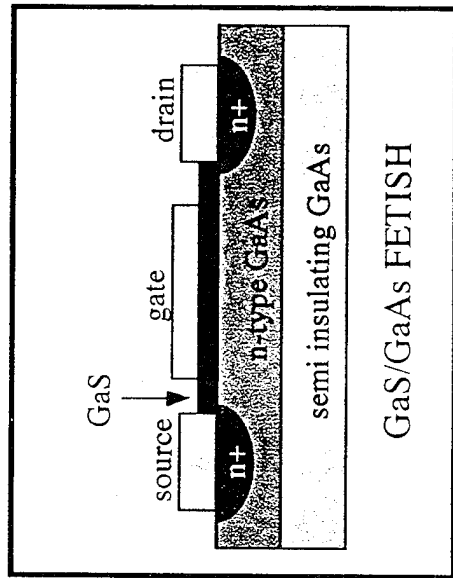
- . Narrow size distribution
- . 30 - 110 nm depending on precursor, temperature, flow rate, and base pressure
- . Polycrystalline
- . Spherical, not domes
- . Snakes stay intact in solution



Why Nano-particles by MOCVD:

- . Vapor phase reaction
- . Non-solvent analog to spray-CVD
- . Molecular fragmentation leads to reactive fragments
- . Weak M-E cage bonds a requisite
- . Thermodynamic structure

Chemically Sensitive Field Effect Transistors (ChemFETs)



The creation of cubic-GaS based GaAs FET (top left) offers the possibility of the fabrication of a chemically sensitive Field Effect Transistors (top right) in which the flow of electrons (and holes) in the channel is controlled by the presence and absence of a chemical (target molecule) on the surface of the gate (bottom left). The modification of the surface of GaS by different linker groups (bottom right) is being investigated.

